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Technology Disclosure Form

SECTION 1: TECHNOLOGY DISCLOSURE DETAILS

RI Technology Disclosure No (To be filled by Res Adm)	2015012
(1) Title of Technology	Nanoinjection molding
(2) Keywords relating to your technology (5-10 keywords)	Molding; Inserts; Nanoinjection molding; Nanoimprint; Nickel electroforming; Hierarchical structures; Iridium coating; Hybrid molds; Nanomanufacturing.
(3) Indicate the category (Annex A) in which your technology falls under	Nanostructured Materials
(4) Brief summary of your technology Attach also a detailed description of your technology.	This invention describes a process called nanoinjection molding to carry out transfer of nanometer-scale patterning onto injected molded products using inserts containing nanometer-sized features. The injection molding inserts were modified with hybrid nanoimprinted templates to enable the nanoinjection molding process. The template can be a basic nanoimprinted structure such as pillars or an array of nanocone structures or a complex three-dimensional hierarchical structure. These can be replicated onto a nickel insert that, after the injection molding process, can then be a part of the overall macro product. The inserts can either be single-sided attached to the cavity side of the molding jig or double sided where the core side of the molding jig can also be attached with the nickel inserts. This will then generate an injection-molded sample that can have nanostructures either on one or both sides of the molded polymer. Nanoinjection molding can be used for the molding of various products where micro and nanostructuring are required for the generation of specific functionalities. Examples include optical lens or helmet visors, which have either one or both sides covered with an array of nanometer cone structures that can greatly enhance the functionality by providing high clarity, anti-UV and superior anti-glare. **Detailed description of technology** **Summary** This invention aims to target a current gap in the injection molding market which is the ability to form multiscale functionalities with high resolutions below < 2 μm on injection molded products or parts using modified inserts. The invention focuses on the modification of injection molding inserts leading to novel inserts which can impart features below 2 μm onto injection-molded products or parts. This will enable the creation of functionalities onto free-form three-dimensional products. The functionality demonstrated in this case is anti-reflectivity (AR) and this design was

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selected due to the complexity and high resolution of the structures. Other functionalities that can be fabricated *via* the nanoinjection molding process include anti-fog, anti-UV, hydrophobicity, iridescence, antibacterial and can even be extended to various other and combination of these functionalities.

These novel inserts that are critical to the nanoinjection molding process are composed of an injection molding insert and also a hybrid insert previously fabricated from nanoimprinting. The hybrid inserts are made from electroformed nickel and coated with iridium. Nickel and iridium have been used to achieve an optimal combination of mechanical properties such as hardness and wear resistance desired in the injection molding process. The process however is not exclusive to hybrid molds. Nickel molds can also be used in the inserts provided the injection molding process conditions are adjusted suitably.

Using a hybrid insert containing anti-reflective nanostructures, we have demonstrated up to 350 shots of an antireflective screen suitable for use in a walkie-talkie set. The lifespan study of the hybrid molds in the inserts is currently on-going.

Background

Injection Molding

Injection molding is a well-established commercial process used for the manufacture of parts or components from thermoplastic and also thermosetting materials. Alongside the extrusion process, it is currently ranked as the prime process used for molding of plastic materials. A typical injection molding process consists of the material to be molded being fed into the hopper. The hopper typically leads to a heated barrel reciprocated by a rotating screw that feeds the material into the molds through pre-defined gates and runners. The pressure, temperature and holding times can be optimized to enable a specific molding criterion to be fulfilled.

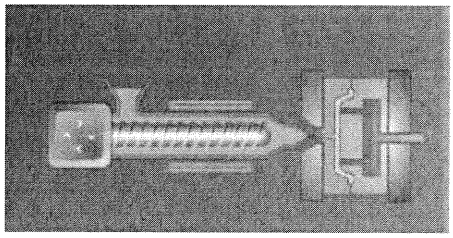

Figure 1: Typical injection molding machine (www.plasticstoday.com)

Injection Molding Inserts

For injection molding, the mold or insert are usually made from hardened steel, aluminium or copper alloys to enable the inserts to withstand the injection molding process conditions. The inserts are usually machined *via* a computer numerical controlled (CNC) machine or using an electrical discharge machine (EDM). A single insert is composed of two parts usually called the injector insert and the ejector insert. These two parts are usually machined to define the final product appearance.

With inserts, an injection molding tool will be able to produce numerous copies of the product, and these copies are defined as 'shots'.

Challenges to injection molding

While injection molding is extremely competitive to other fabrication techniques, the process itself still suffers from inherent limitations where the resolution of the parts and components to be produced is in the micrometer range and below. While there have been efforts mainly by the biomedical product makers to carry out molding in the nanorange, this is still limited to components. As of yet, the nanostructuring to yield surface textures onto injection-molded products is still in its infancy.

We have previously demonstrated the role of various nanostructures on surfaces such as plastics to elicit properties like anti-reflectivity, anti-fog, etc. These demonstrated applications have been proven on two-dimensional films and not on a free-form three-dimensional product. In this case, we have opted to modify the injection molding inserts with a nanoimprint template to yield a hybrid insert capable of carrying out nanoinjection molding to transfer high resolution features (<200 nm) onto injection molded free-form three-dimensional products.

Results

Fabrication of Nickel Mold Inserts

Nickel mold inserts with micro and nano structures can be fabricated using nanoimprint technology. The pattern transfer is essentially from an imprinted polymer that can be used as a platform template to be electroformed into a thick nickel mold. This proposed invention relies on a novel lamination plus planarization methods that flatten and bond a soft template with patterns on its surface to a highly flat solid surface, typically a silicon wafer, without damage or physical contact to the patterns. Any complex feature such as moth's eye or hierarchical structures can be translated and replicated onto a nickel mold with a good uniform flatness. Therefore, the textured surface technology that has been demonstrated by nanoimprinting which can produce functional properties such as anti-wetting, super-hydrophobicity and anti-reflection can be translated onto the nickel inserts. This, therefore, brings forth a new dimension of producing biomimetic structures onto a three-dimensional scale by injection molding. Mold replication from templates is needed to produce functional surfaces at industrially relevant throughput. In mold replication, it is important that the template used is extremely flat and uniform. Without this, misalignment, defects, breakage and low fidelity of replicated mold structures ultimately cannot provide the desired surface functions. The method presented here overcomes challenges in soft mold replication leading to fabrication high quality robust and reusable inserts for injection molding. The method utilizes a spin-coated epoxy based intermediate layer to laminate a soft mold/template onto a silicon wafer. To ensure a highly conformal contact with the wafer, an epoxy glue is diluted and spin-coated with optimized thickness to provide strong bonding as well as flatness. The final assembly is sputter-coated by a thin metal film used as a seed

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layer for subsequent electroplating to fabricate a high quality nickel mold insert consisted of negative replica of the template patterns with superior physical characteristics of flatness, smoothness, uniformity and high fidelity.

For simple structure templates such as pillars, holes or conical structures, their replication had been previously carried out by direct nanoimprinting from a master mold. However, to make a complex hierarchical imprinted template, we make used of a prior art that uses a dual-stage imprinting to form primary and secondary structures. For illustration, we will demonstrate making a nanopillar on a lens structure.

To prepare a template with hierarchical structures, we utilized two stages of sequential nanoimprinting to form the primary (micron-scale) and secondary (nano-scale) imprint structures at two non-planar levels onto a thin sheet of polycarbonate (PC) over large areas. The templates were used for further tests of our technology by flatly gluing the imprinted film onto a silicon substrate followed by a nickel electroforming process to form the mold. Figure 2 shows the schematics of the process flow.

Preparation of PC template with hierarchical structures:

1) In the first step, a silicon mold with a close pack array of microlens with diameters of 7.8 μm, pitch of 7.8 μm and a height of 5.5 μm was used for imprinting onto a 250 μm thin polycarbonate (PC) sheet to form the primary structures which has a semi-cone shape. The imprinting is carried out using temperature of 180 °C and pressure of 40 bar pressure for 300 sec. Figure 3a shows the imprinted profile of the PC.
2) Next, the secondary structure is formed using another silicon mold that has an array of 300 nm square holes with aspect ratio of 1 and a pitch size of 600 nm. The imprinted version of PC in this case is a hierarchical structure where the secondary features are 300 nm square pillars as shown in the SEM images of Figure 3b.This imprinting is done at the condition of 150 °C at 20 bar pressure and a duration of 300 sec.

Template lamination and electroplating:

The imprinted PC film with hierarchical structures resembles the as-received polymer film with similar flexibility and non-uniformity. Therefore, if it is used for electroforming of a nickel mold, it may result in a non-uniform wavy mold with misalignment of the structures on its surface. In order to have good fidelity of the nickel replica, the imprinted PC template must maintain a high degree of flatness throughout the whole electroforming process.

As the conditions of the nickel electrolyte during electroforming are constantly maintained at an acidic level and a high temperature of over 50 °C over a long

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period; it is essential that the whole assembly of PC film is strongly bonded onto the highly flat surface of silicon wafer, is gap free and must be able withstand the bath conditions while maintaining the flatness. The PC film is assembled onto the wafer with SU8. The usual processing conditions for SU8 are followed.

Electroforming of the nickel mold:

In this process, we have adopted nickel vanadium (NiV) alloy as the conductive seed layer due to the fact that NiV does not oxidize in air and it eases the delamination process. The deposition of the NiV seed layer on the patterned wafer was done by DC magnetron sputtering at 100 W with 10 sccm of Ar gas. Approximately 30 nm of NiV was deposited.

Nickel electroforming was conducted in a Technotrans AG, RD200 plating system containing a nickel sulfamate bath with sodium-dodecyl-ether-sulphamate as the wetting agent without organic additives. The composition of the bath was: 89 ± 3 g/l of pure Ni^{2+}, i.e., 380 ± 10 g/l nickel sulfamate, $NiCl_2$ ~ 10 g/l, 40 g/l boric acid as a buffer and an approximately 0.06 g/l of an anion active wetting agent. The temperature of the bath was held at above 50 °C. In this electrodeposition, a low current density has to be maintained to ensure a certain degree of high hardness.

After nickel electroforming, the PC template was completely dissolved by soaking in dichloromethane (DCM - CH_2Cl_2) thus retaining the structural fidelity of the hierarchical structures. Figure 3 shows the SEM images of the electroformed nickel mold with negative replica structures.

Lastly, the nickel mold can also be sputtered with metals such as iridium to impart additional hardness to the insert. The final insert is then trimmed into the required size and dimensions as required to be fitted into the injection molding jig.

Figure 3 and 4 show the SEM images of the various types of inserts suitable for use in the nanoinjection molding process.

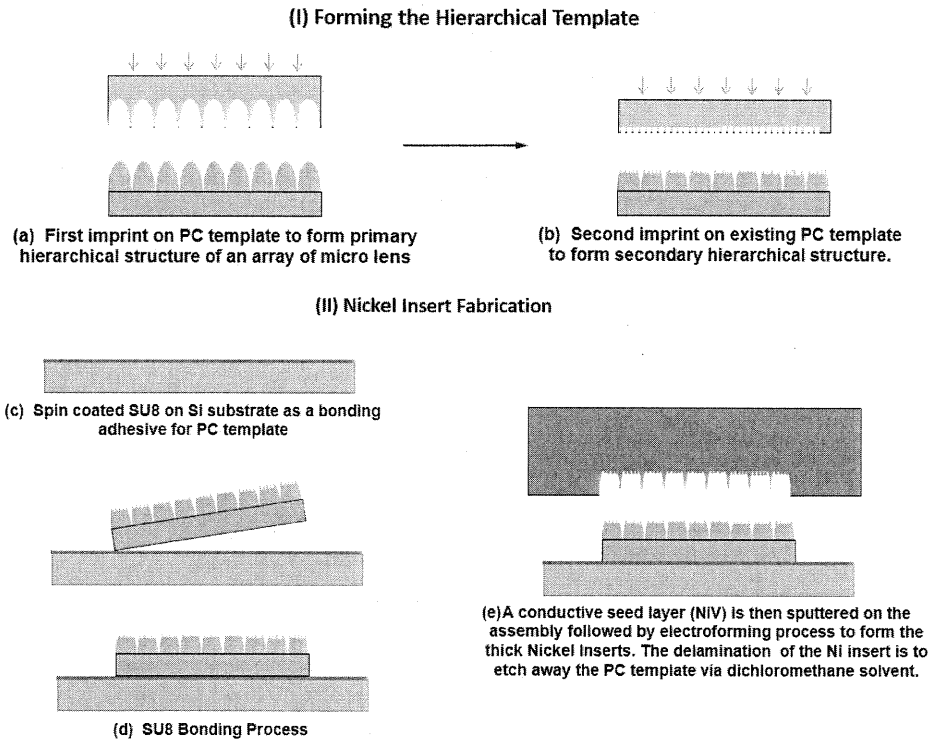

Figure 2: Schematics of the process flow for making the hierarchical structure

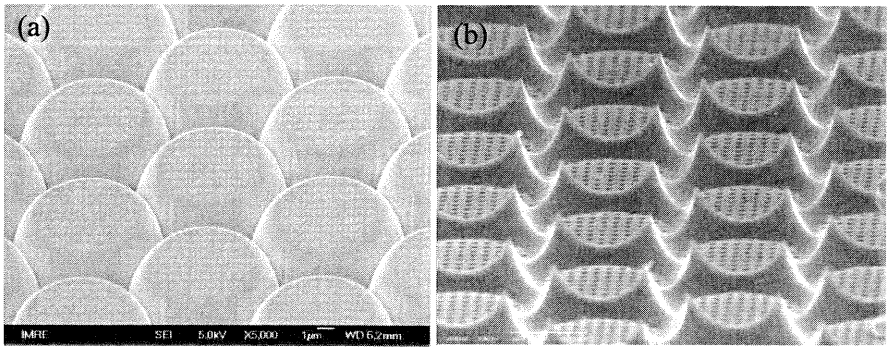

Figure 3: SEM of the hierarchical structures. (a) Imprinted polymer template, and (b) its corresponding nickel replica Insert.

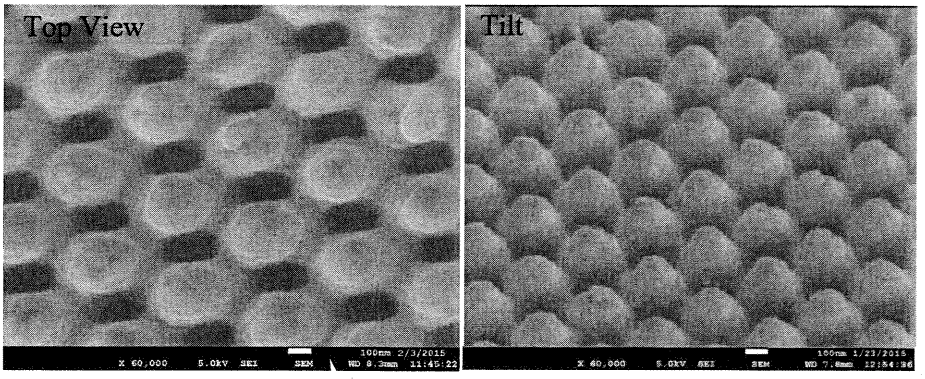

Figure 4: SEM of the nickel inserts containing anti-reflection structures.

The replicated nickel inserts containing micro- and nanostructures can be incorporated into a steel insert platform by using a hidden magnetic disc that firmly hold the inserts in the steel platform. The thickness of the insert can be in varied according to the requirement of the process and can be tailored very precisely into an existing tooling jig by means of wire cutting. Figure 5 shows the Nickel inserts been mounted onto the steel jig as well as the dual Nickel inserts on the core and cavity side of the molding jig.

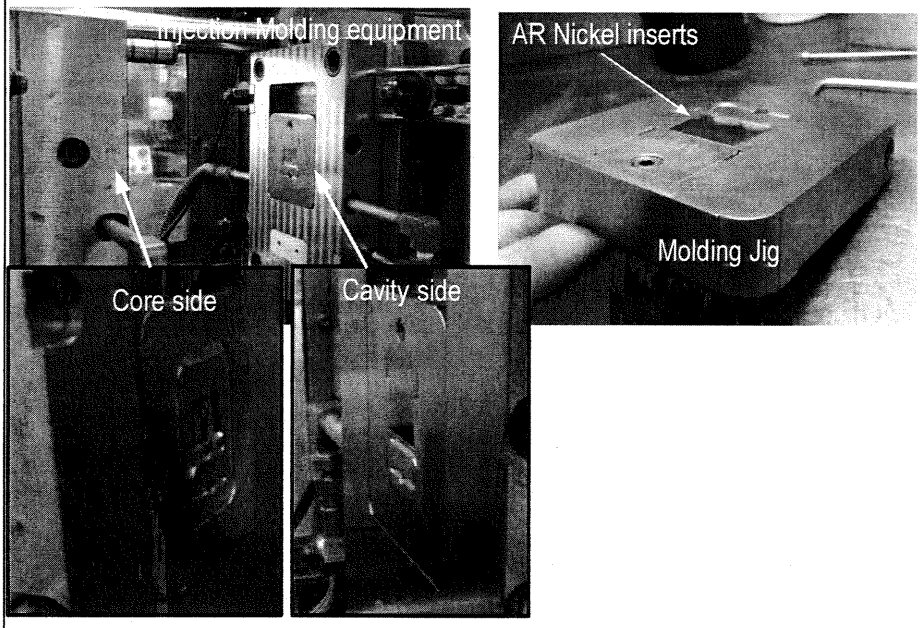

Figure 5: Illustration of the dual Nickel inserts on the Molding jig

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Nanoinjection Molding process

To demonstrate the nanoinjection molding using our nickel inserts, we used a moth's eye structure that consists of closely pack hexagonally arrayed 250 nm cone structures. Figure 4 shows the SEM images of the nickel inserts containing the anti-reflection structures, with a thin layer to iridium coated on top.

The nanoinjection molding process is controlled by four main parameters. These parameters will ultimately determine whether a good filling of the molten polymer can be achieved. A good filling will yield a good replication of the inserts. The four parameters are the (1) temperature of the polymer melt, (2) the injection pressure, (3) the injection speed and lastly, (4) the holding time required for the polymer melt to fill up the structures before the polymer is allowed to cool down. As the mold insert is made from nickel, the strategy here is to optimise an injection molding condition that is not too harsh that will degrade and shorten the life time of metal insert. In our study, we have defined a process window where the injection pressure and the injection speed has to be less than 100 MPa and 100 mm/s, respectively, in order to preserve the life span of the nickel inserts.

Figure 6 shows the SEM of the injection molded product with the anti-reflection structures. Visual inspection in Figure 7 shows a deep blue color at slightly oblique angles which suggests that the anti-reflection structures have been reproduced faithfully from the inserts. The SEM images confirm the well-defined structure based on the optimized injection molding conditions at 320 °C polymer melt temperature, injection pressure at 100 MPa, injection speed at 75 mm/s and a longer holding time of 16 sec for a polycarbonate feed.

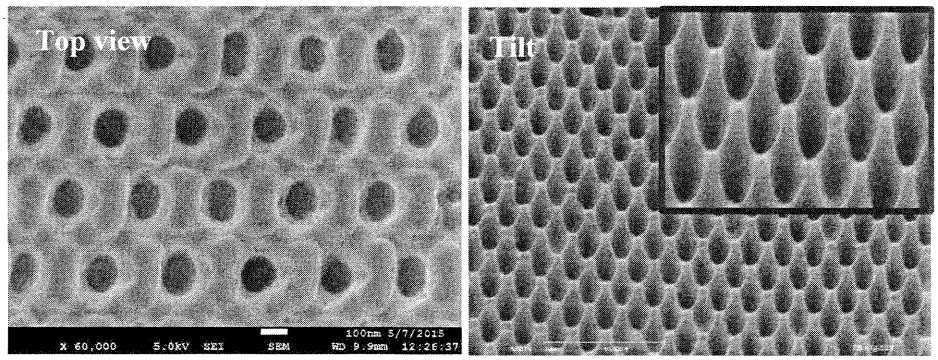

Figure 6: SEM images of the optimized injection molded anti-reflection structure replica.

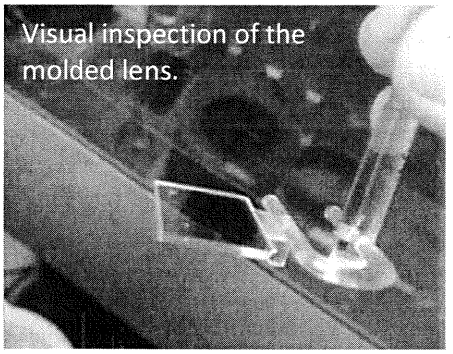

Figure 7: Visual inspection of an injection molded sample where the anti-reflection structure displays a deeper blue color when viewed from an oblique angle.

Figure 8 depicts transmission measurements done on the injection-molded lens fabricated at various experimental conditions. The molded samples were randomly chosen for the transmission test. As a comparison, another sample was also chosen from a non-optimised process run. The non-optimized sample refers to an injection molding run where the polymer filling of the anti-reflection structure was not complete. The results do show a distinct difference between the two types of samples. An injection molded lens with a good replica of anti-reflection structures displays higher transmission level with improvement at around 5% within the visible light spectrum. For a lens with double-sided anti-reflection structures, we would expect the transmission to go as high as 99%.

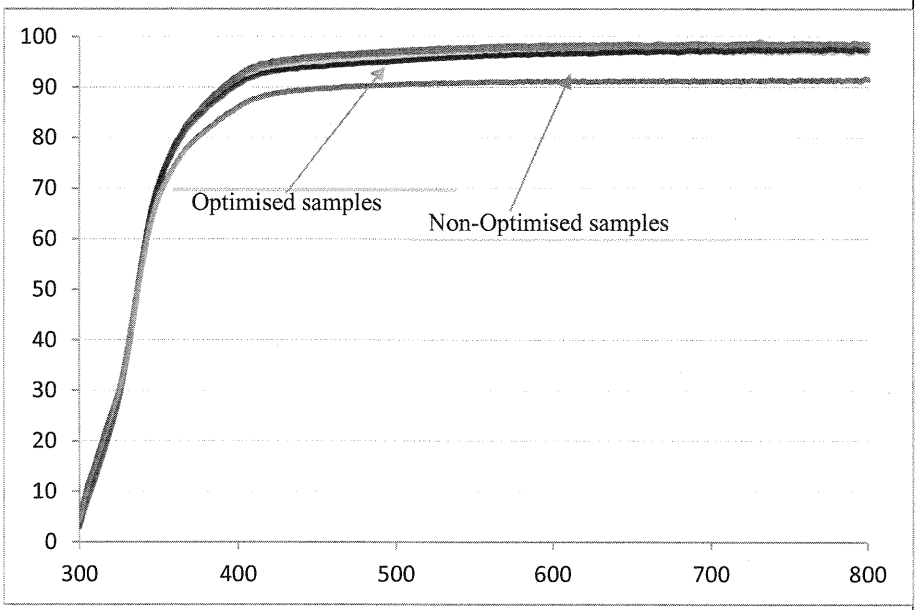

Figure 8: Transmission study of injection molded lenses prepared at various experimental conditions.

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(5) Key technical features (excluding advantages such as cost, efficiency). (e.g. A semiconductor structure.... An isolated nucleotide sequence ... A method of....)	• Nanoinjection molding – fabrication of specific high-resolution features onto injection molded components. • Hybrid nanoinjection molding inserts. • High resolution inserts <200 nm. • High aspect ratio structures fabricated on inserts. • Mixed resolution structures fabricated on inserts. • Inserts on both side of the molding jig.

(5) Novelty / Non-obviousness Highlight the novelty and non-obviousness of your technology disclosure in view of prior art in which you have cited. Provide the details in separate sheets if necessary.	**Novelty** 1) High-resolution features <200 nm. 2) Molding process suitable for <200 nm. 3) Using nanoimprinted template to achieve nickel mold inserts for injection molding. 4) Able to translate complex hierarchical structure that has functional properties to be used in an injection molding process. 5) Coating of iridium on the nickel surface to enhance the life time of nickel mold. 6) Double sided inserts on the molding jig **Non-obviousness** 1) Modification of the inserts *via* nanoimprinting templates. 2) Fabrication of nanotextures on injection molded products.

INFORMATION SHEET

Title Of Invention:	Nanoinjection Molding
Filing Country:	Non-fully drafted Singapore patent application
Priority Claim:	Nil
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